



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 369 436 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
15.05.1996 Bulletin 1996/20

(51) Int Cl.⁶: **C08L 23/04, C08F 297/08**

(21) Application number: **89121160.9**

(22) Date of filing: **15.11.1989**

(54) Process for the in situ blending of polymers

In situ-Mischungsverfahren für Polymere

Procédé pour le mélange in situ de polymères

(84) Designated Contracting States:
AT BE DE ES FR GB GR IT NL SE

(30) Priority: **16.11.1988 US 271639**

(43) Date of publication of application:
23.05.1990 Bulletin 1990/21

(73) Proprietor: **UNION CARBIDE CHEMICALS AND
PLASTICS COMPANY INC.**
(a New York corporation)
Danbury Connecticut 06817-0001 (US)

(72) Inventors:
• **Lee, Kiu Hee**
South Charleston West Virginia 25303 (US)

• **Samuels, Sari Beth**
North Woodmere New York 11581 (US)
• **Karol, Frederick John,**
Belle Mead New Jersey 088520 (US)

(74) Representative: **Barz, Peter, Dr. et al**
Patentanwalt
Kaiserplatz 2
D-80803 München (DE)

(56) References cited:
EP-A- 0 022 376 EP-A- 0 027 386
EP-A- 0 131 268 EP-A- 0 298 453
DE-A- 1 569 220 DE-A- 2 920 729
US-A- 3 914 342

EP 0 369 436 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

This invention relates to a process for polymerization whereby resins are manufactured and blended in situ.

There has been a rapid growth in the market for linear low density polyethylene (LLDPE), particularly resin made under mild operating conditions, typically at pressures of 0.69 to 2.1 MPa (100 to 300 psi) and reaction temperatures of less than 100°C. This low pressure process provides a broad range of LLDPE products for film, injection molding, extrusion coating, rotational molding, blow molding, pipe, tubing, and wire and cable applications. LLDPE has essentially a linear backbone with only short chain branches, about 2 to 6 carbon atoms in length. In LLDPE, the length and frequency of branching, and, consequently, the density, is controlled by the type and amount of comonomer used in the polymerization. Although the majority of the LLDPE resins on the market today have a narrow molecular weight distribution, LLDPE resins with a broad molecular weight distribution are available for a number of applications.

LLDPE resins designed for commodity type applications typically incorporate 1-butene as the comonomer. The use of a higher molecular weight alpha-olefin comonomer produces resins with significant strength advantages relative to 1-butene copolymers. The predominant higher alpha-olefins in commercial use are 1-hexene, 1-octene, and 4-methyl-1-pentene. The bulk of the LLDPE is used in film products where the excellent physical properties and drawdown characteristics of LLDPE film makes this film well suited for a broad spectrum of applications. Fabrication of LLDPE film is generally effected by the blown film and slot casting processes. The resulting film is characterized by excellent tensile strength, high ultimate elongation, good impact strength, and excellent puncture resistance.

These properties together with toughness are enhanced when the polyethylene is of high molecular weight. However, as the molecular weight of the polymer increases, the processability of the resin usually decreases. By providing a blend of polymers, the properties characteristic of high molecular weight resins can be retained and processability, particularly extrudability, can be improved.

Three major strategies have been proposed for the production of resins of this nature. One is post reactor or melt blending, which suffers from the disadvantages brought on by the requirement of complete homogenization and attendant high cost. A second is the direct production of resins having these characteristics via a single catalyst or catalyst mixture in a single reactor. Such a process would provide the component resin portions simultaneously in situ, the resin particles being ultimately mixed on the sub-particle level. In theory, this process should be the most rewarding, but, in practice, it is difficult to achieve the correct combination of catalyst and process parameters necessary to obtain the wide diversity of molecular weights required. The third strategy makes use of multistage reactors, the advantage being that a quite diverse average molecular weight can be produced in each stage, and yet the homogeneity of the single reactor process can be preserved. Furthermore, two or more reactors running under their own set of reaction conditions permit the flexibility of staging different variables. To this end, many versions of multistage reactor processes have been offered, but optimization has been elusive.

EP-A-298 453, a document relevant under Art. 54(3) EPC, relates to a process for the production of impact polypropylene copolymers wherein an ethylene/propylene copolymer is incorporated into a matrix of propylene homopolymer or copolymer and wherein the matrix is prepared in a first reactor and is then transferred to a second reactor where the copolymer is made. The titanium-based catalyst employed in said process is used as such, i.e., without support.

EP-A-22 376 is concerned with a process for preparing a fish-eye-free chemically blended composition of non-elastomeric ethylene resins. Critical features of said process are, i.e., the ethylene contents and the intrinsic viscosities of the ethylene/alpha-olefin copolymers employed and of the resulting blend and the weight ratio of the copolymers.

EP-A-27 386 discloses a process for producing a chemically blended propylene resin composition having an ethylene content of 1 to 40 mole-%. Said process comprises a pre-polymerization step and a multiplicity of subsequent polymerization steps.

EP-A-131 268 describes a process for the preparation of propylene-ethylene block copolymers wherein a propylene homopolymer is first prepared and propylene and ethylene are then copolymerized in a second polymerization zone in the presence of said polypropylene.

DE-A-1 569 220 relates to the blending of independently and separately prepared polyolefins, preferably in solution.

An object of this invention is to provide an optimized process for the multistage in situ blending of polymers to provide the desired properties as well as processability.

Other objects and advantages will become apparent hereinafter.

According to the present invention, a process for the in situ blending of polymers is provided, said process involving the preparation of a high melt index ethylene copolymer in a high melt index reactor and the blending of a low melt index ethylene copolymer with said high melt index ethylene copolymer in a low melt index reactor and comprising continuously contacting, under polymerization conditions, a mixture of ethylene and at least one alpha-olefin having at least 3 carbon atoms with a catalyst in the gas phase in at least two fluidized bed reactors connected in series, said catalyst comprising:

- (i) a silica supported complex consisting essentially of magnesium, titanium, a halogen, and an electron donor;
 (ii) at least one activator compound for the complex having the formula $AlR''_eX'_fH_g$ wherein X' is Cl or OR''' ; R'' and R''' are saturated aliphatic hydrocarbon radicals having 1 to 14 carbon atoms and are alike or different; f is 0 to 1.5; g is 0 or 1; and $e + f + g = 3$; and
 5 (iii) a hydrocarbyl aluminum cocatalyst, the polymerization conditions being such that a high melt index ethylene copolymer having a melt index in the range of from 0.2 to 600 grams per 10 minutes is formed in at least one high melt index reactor and a low melt index ethylene copolymer having a melt index which is lower than that of the high melt index ethylene copolymer and is in the range of from 0.001 to 1.0 gram per 10 minutes is formed in at least one low melt index reactor, each copolymer having a melt flow ratio in the range of from 22 to 70, and being
 10 admixed with active catalyst, with the proviso that:
 (a) the mixture of copolymer of ethylene and active catalyst formed in one reactor in the series is transferred to the immediately succeeding reactor in the series;
 (b) in the reactor in which the low melt index copolymer is made:
 15 (1) the alpha-olefin is present in a ratio of from 0.1 to 3.5 moles of alpha-olefin per mole of ethylene; and
 (2) hydrogen is present in a ratio of from 0.001, particularly from 0.005, to 0.5 mole of hydrogen per mole of combined ethylene and alpha-olefin;
 (c) in the reactor in which the high melt index copolymer is made:
 20 (1) the alpha-olefin is present in a ratio of from 0.02, particularly from 0.1, to 3.5 moles of alpha-olefin per mole of ethylene; and
 (2) hydrogen is present in a ratio of from 0.05, particularly from 0.5, to 3 moles of hydrogen per mole of combined ethylene and alpha-olefin; and
 25 (d) additional hydrocarbyl aluminum cocatalyst is introduced into each reactor in the series following the first reactor in an amount sufficient to restore the level of the activity of the catalyst transferred from the preceding reactor in the series to about the initial level of activity in the first reactor.
- 30 The titanium based complex (i) is exemplified by a complex having the formula $Mg_aTi(OR)_bX_c(ED)_d$ wherein R is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR group is alike or different; X is Cl, Br, or I, or mixtures thereof; ED is an electron donor, which is a liquid Lewis base in which the precursors of the titanium based complex are soluble; a is 0.5 to 56; b is 0, 1, or 2; c is 1 to 116, particularly 2 to 116; and d is 2 to 85. This complex and a method
 35 for its preparation are disclosed in US-A-4,303,771.
- The titanium compound, which can be used in the above preparations, has the formula $Ti(OR)_aX_b$ wherein R and X are as defined for component (i) above; a is 0, 1 or 2; b is 1 to 4; and $a+b$ is 3 or 4. Suitable compounds are $TiCl_3$, $TiCl_4$, $Ti(OC_6H_5)Cl_3$, $Ti(OCOCH_3)Cl_3$ and $Ti(OCOC_6H_5)Cl_3$.
- The magnesium compound has the formula MgX_2 wherein X is as defined for component (i) above. Suitable ex-
 40 amples are $MgCl_2$, $MgBr_2$, and MgI_2 . Anhydrous $MgCl_2$ is a preferred compound. 0.5 to 56, and preferably 1 to 10, moles of the magnesium compound are used per mole of titanium compound.
- The electron donor used in the catalyst composition is an organic compound, liquid at temperatures in the range of 0°C to 200°C. It is also known as a Lewis base. The titanium and magnesium compounds are both soluble in the electron donor.
- 45 Electron donors can be selected from alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl and cycloalkyl ethers, and mixtures thereof, each electron donor having 2 to 20 carbon atoms. Among these electron donors, the preferred are alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; dialkyl, diaryl, and alkaryl ketones having 3 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms. The most preferred electron donor is tetrahydrofuran.
- 50 Other examples of suitable electron donors are methyl formate, ethyl acetate, butyl acetate, ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethyl formate, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, and ethyl propionate.
- The activator compound is represented by the formula $AlR''_eX'_fH_g$ wherein X' is Cl or OR''' ; R'' and R''' are saturated aliphatic hydrocarbon radicals having 1 to 14 carbon atoms and are alike or different; f is 0 to 1.5; g is 0 or 1; and $e + f + g = 3$. Examples of suitable R'' , R' , R'' , and R''' radicals are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, 2-methylpentyl, heptyl, octyl, isooctyl, 2-ethylhexyl, 5,5-dimethylhexyl, nonyl, decyl, isodecyl, undecyl, dodecyl, cyclohexyl, cycloheptyl, and cyclooctyl. Examples of suitable R and R' radicals are phenyl, phenethyl, methoxyphenyl, benzyl, tolyl, xylyl, naphthyl, methylnaphthyl.

Some examples of useful activator compounds are as follows: triisobutylaluminum, trihexylaluminum, di-isobutylaluminum hydride, dihexylaluminum hydride, di-isobutylhexylaluminum, trimethylaluminum, triethylaluminum, diethylaluminum chloride, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$, and $\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$. The preferred activators are triethylaluminum, triisobutylaluminum, and diethylaluminum chloride. The cocatalyst can be selected from among those compounds suggested as activators, which are hydrocarbyl aluminum compounds. Triethylaluminum and triisobutylaluminum are preferred cocatalysts.

Silica is the support for the titanium-based complex and may also be silica/alumina mixtures, silica modified with an organoaluminum compound such as triethylaluminum, and silica modified with diethylzinc. A typical silica support is a solid, particulate material essentially inert to the polymerization. It is used as a dry powder having an average particle size of 10 to 250 μm and preferably 30 to 100 μm ; a surface area of at least 3 square meters per gram and preferably at least 50 square meters per gram; and a pore size of at least 8 nm (80 Angstroms) and preferably at least 10 nm (100 Angstroms). Generally, the amount of support used is that which will provide 0.01 to 0.5 millimole of transition metal per gram of support and preferably 0.2 to 0.35 millimole of transition metal per gram of support. Impregnation of the abovementioned catalyst precursor into silica is accomplished by mixing the complex and silica gel in the electron donor solvent followed by solvent removal under reduced pressure.

The activator can be added to the titanium complex either before or during the polymerization reaction. It is usually introduced before polymerization, however. In each reactor, the cocatalyst can be added either before or during the polymerization reaction; however, it is preferably added neat or as a solution in an inert solvent, such as isopentane, to the polymerization reaction at the same time as the flow of ethylene, alpha-olefin, and hydrogen is initiated.

Useful molar ratios are as follows:

Titanium based catalyst	Broad	Preferred
1. Mg:Ti	0.5:1 to 56:1	1.5:1 to 5:1
2. Mg:X	0.005:1 to 28:1	0.075:1 to 1:1
3. Ti:X	0.01:1 to 0.5:1	0.05:1 to 0.2:1
4. Mg:ED	0.005:1 to 28:1	0.15:1 to 1.25:1
5. Ti:ED	0.01:1 to 0.5:1	0.1:1 to 0.25:1
6. activator:Ti	0.5:1 to 50:1	1:1 to 5:1
7. cocatalyst:Ti	0.1:1 to 200:1	10:1 to 100:1
8. ED:Al	0.05:1 to 25:1	0.2:1 to 5:1

The polymerization in each reactor is conducted in the gas phase using a continuous fluidized bed process. A typical fluidized bed reactor is described in US-A-4,482,687. As noted, the reactors are connected in series. While two reactors are preferred, three or more reactors can be used to further vary the molecular weight distribution. As more reactors are added producing different average molecular weight distributions, however, the sharp diversity of which two reactors are capable becomes less and less apparent. It is contemplated that these additional reactors could be used to produce copolymers with melt indices intermediate to the high and low melt indices previously referred to.

The high melt index is in the range of 0.2 to 600 grams per 10 minutes. The low melt index is in the range of 0.001 to 1.0 gram per 10 minutes and is preferably in the range of 0.01 to 0.2 gram per 10 minutes. The melt flow ratio is, however, about the same in both reactors, i.e., in the range of 22 to 70.

Melt index is determined under ASTM D-1238, Condition E. It is measured at 190°C and reported as grams per 10 minutes.

Melt flow ratio is the ratio of flow index to melt index. Flow index is determined under ASTM D-1238, Condition F. It is measured at 10 times the weight used in determining the melt index.

The titanium complex including the activator, the cocatalyst, the ethylene monomer, any comonomers, and hydrogen, if any, are continuously fed into each reactor and ethylene copolymer and active catalyst are continuously removed from one reactor and introduced into the next reactor. The product is continuously removed from the last reactor in the series.

The alpha-olefin used to produce the polyethylene can have 3 to 10 carbon atoms and preferably has 3 to 8 carbon atoms. Preferred alpha-olefins are 1-butene, propylene, 1-hexene, 1-octene, 4-methyl-1-pentene. The density of the ethylene copolymer can be varied depending on the amount of alpha-olefin comonomer added and upon the particular comonomer employed. The greater the percent of alpha-olefin comonomer, the lower the density. The density of the polyethylene is 0.860 to 0.965, particularly to 0.955, gram per cubic centimeter.

The mole ratio of alpha-olefin to ethylene used to obtain the high melt index is in the range of 0.02:1 to 3.5:1, preferably 0.1:1 to 3.5:1. The ratios depend upon the amount of hydrogen, the amount of comonomer, and the density and melt index desired.

Both the comonomer and hydrogen can act as chain terminators. In the subject process, hydrogen is required in both the high melt index and the low melt index reactor.

The mole ratio of hydrogen to combined ethylene and alpha-olefin in the high melt index reactor is in the range of 0.05:1 to 3:1, and particularly preferred is in the range of about 0.5:1 to 2:1. The mole ratio of hydrogen to combined ethylene and alpha-olefin in the low melt index reactor is in the range of 0.001:1 to 0.5:1, preferably 0.005:1 to 0.5:1, and particularly preferred is in the range of 0.01:1 to 0.3:1.

The fluidized bed polymerizations are conducted at a temperature below the sintering temperature of the product. The operating temperature is generally in the range of 10°C to 115°C. Preferred operating temperatures will vary depending upon the density desired. Low density polyethylenes ranging in density from 0.860 to 0.910 gram per cubic centimeter are preferably produced at an operating temperature of 10°C to 80°C. The higher temperatures are used to achieve higher densities.

The high melt index reactor can be operated in the range of 30°C to 105°C and is preferably operated in the range of 75°C to 90°C. The low melt index reactor can be operated in the same range, the higher density resins utilizing the high end of the range. Insofar as pressures are concerned, the high melt index reactor can be operated at 0.69 to 6.9 MPa gauge (100 to 1000 psig) and preferably at 0.69 to 2.4 MPa gauge (100 to 350 psig). The low melt index reactor can be operated at similar pressures.

Other conditions in the reactors can be about as follows:

LOW MELT INDEX REACTOR		
	BROAD RANGE	PREFERRED RANGE
1. residence time (hour):	1 to 10	2 to 5
2. fluidizing gas velocity, m per sec. (foot per second):	0.3 to 1.05 (1 to 3.5)	0.45 to 0.75 (1.5 to 2.5)
3. low melt index copolymer (percent by weight based on total copolymer produced in two reactors):	10 to 90	40 to 70

HIGH MELT INDEX REACTOR		
	BROAD RANGE	PREFERRED RANGE
1. residence time (hours):	1 to 10	2 to 5
2. fluidizing gas velocity, m per sec. (foot per second):	0.3 to 1.05 (1 to 3.5)	0.45 to 0.75 (1.5 to 2.5)
3. high melt index copolymer (percent by weight based on total copolymer produced in two reactors):	10 to 80	20 to 75

An example of properties obtained from a two reactor (or two stage) process:

1. First reactor copolymer:
Melt Index = 250 grams/10 min
Density = 0.930 gram/cc.
Melt Flow Ratio = 25
2. Second reactor copolymer
Melt Index = 0.1 to 1.0 grams/10 min
Density = 0.915 to 0.918 gram/cc
Melt Flow Ratio = 25
3. Homogeneous mixture of both copolymers from second reactor:
Melt Index: 0.3 to 1.3 grams/10 min
Density = 0.915 to 0.926 gram/cc
Melt Flow Ratio = 50 to 68

The first reactor is generally smaller in size than the second reactor because only a portion of the polymer is made in the first reactor. The mixture of copolymer and an active catalyst is usually transferred from the first reactor to the second reactor via an interconnecting device using nitrogen or second reactor recycle gas as a transfer medium.

A typical fluidized bed reactor can be described as follows:

The bed is usually made up of the same granular resin that is to be produced in the reactor. Thus, during the course

of the polymerization, the bed comprises formed polymer particles, growing polymer particles, and catalyst particles fluidized by polymerization and modifying gaseous components introduced at a flow rate or velocity sufficient to cause the particles to separate and act as a fluid. The fluidizing gas is made up of the initial feed, make-up feed, and cycle (recycle) gas, i.e., comonomers and, if desired, modifiers and/or an inert carrier gas.

The essential parts of the reaction system are the vessel, the bed, the gas distribution plate, inlet and outlet piping, a compressor, cycle gas cooler, and a product discharge system. In the vessel, above the bed, there is a velocity reduction zone, and in the bed, a reaction zone. Both are above the gas distribution plate.

Advantages of the product of subject process are the homogeneity and uniformity of the physical properties throughout the blend and the high strength and toughness obtained without processing difficulty.

The invention is illustrated by the following examples.

EXAMPLES 1 to 3

The examples are carried out in accordance with the procedure described above.

A catalyst is prepared from a mixture of $\text{MgCl}_2/\text{TiCl}_3/0.33\text{AlCl}_3$ /tetrahydrofuran supported on silica that has been dehydrated at 600°C under a nitrogen atmosphere. [Note: one commercial form of TiCl_3 contains an aluminum impurity due to the way the TiCl_4 is reduced to TiCl_3 . This form is used in the examples. A form of TiCl_3 , which does not contain aluminum, can also be used, e.g., a form known as hydrogen-reduced TiCl_3 .] The support is treated with triethyl aluminum to passivate the surface through reaction with the remaining surface silanol groups, and with diethyl aluminum chloride and tri-n-hexyl aluminum to moderate the kinetic reaction behavior of the catalyst and promote good resin particle shape, i.e., substantial absence of particle which are "blown open" and a minimum of hollow particles.

The catalyst is made in a two-step process. The magnesium chloride/titanium chloride/tetrahydrofuran salt is impregnated into the silica support from the tetrahydrofuran solvent. The composition of the catalyst precursor is as follows:

component	percent by weight
TiCl_3	5.97
MgCl_2	8.58
tetrahydrofuran	15.00
support (silica treated with $\text{Al}(\text{C}_2\text{H}_5)_3$)	70.45
	<u>100.00</u>

Analysis of the catalyst precursor:

component	percent by weight
Ti	1.437
Mg	2.188
Al	1.182
Cl	10.650
tetrahydrofuran	15.000
silica	69.543
	<u>100.000</u>

The precursor is contacted with diethyl aluminum chloride and tri-n-hexyl aluminum in an isopentane solvent; the residue is dried, and the catalyst is ready for use in the first reactor. The diethyl aluminum chloride and tri-n-hexyl aluminum are added in amounts based on the tetrahydrofuran content. The diethyl aluminum chloride is added first at a mole ratio of 0.2/1 based on tetrahydrofuran. The tri-n-hexyl aluminum is then added at a mole ratio of 0.2:1 based on the tetrahydrofuran. The finished catalyst is dried to a free flowing powder having the following composition:

component	percent by weight
Ti	1.24
Mg	1.888
Al (total)	3.43

Continuation of the Table on the next page

(continued)

component	percent by weight
Cl (from Ti and Mg)	9.19
tetrahydrofuran	12.94
diethyl aluminum chloride	4.31
tri-n-hexyl aluminum	10.14

Polymerization is initiated in the first reactor by continuously feeding the above catalyst and a cocatalyst, triethylaluminum (TEAL), into a fluidized bed of polyethylene granules together with the gaseous comonomers and hydrogen. The TEAL is dissolved in isopentane (5 percent by weight TEAL). The resulting copolymer mixed with active catalyst is withdrawn from the first reactor and transferred to the second reactor using nitrogen as a transfer medium. The second reactor also has a fluidized bed of polyethylene granules. Again gaseous comonomers and hydrogen are introduced into the second reactor where they come in contact with the copolymer and catalyst from the first reactor. Additional cocatalyst is also introduced. The copolymer product is continuously removed. Variables with respect to catalyst and conditions as well as the properties of the resin product are set forth in the Table.

Table

Example	1	2	3
Catalyst	Reactor I	Reactor I	Reactor II
Ti loading (millimole per gram of support)	Reactor II	Reactor II	Reactor II
Mg/Ti (atomic ratio)	0.25	0.25	0.25
Ti (weight % based on weight of total catalyst)	3.0	3.0	3.0
Al (weight % based on weight of total catalyst)	1.0	0.94	1.0
TEAL (weight % based on weight of silica)	2.88	2.73	2.87
Reaction Conditions	5	5	5
Reactor temperature (°C)	86	86	82
Reactor pressure MPa (psia)	2.168 (314.7)	2.168 (314.7)	2.168 (314.7)
Hydrogen/ethylene (mole ratio)	1.21	1.47	1.93
Comonomer	1-butene	1-butene	1-butene
Comonomer/ethylene (mole ratio)	0.319	0.317	0.131
Ethylene partial pressure (psia)	0.56(82)	0.54(79)	0.50(73)
Nitrogen (% of total reactor pressure)	33	30	21
Fluidization velocity m/s (feet per second)	0.54(1.8)	0.54(1.8)	0.54(1.8)
Percent of total production	62	30	39

Table (continued)

Example	1		2		3	
	Reactor I	Reactor II	Reactor I	Reactor II	Reactor I	Reactor II
Fluidized bed weight kg (pounds)	27(60)	63(140)	27(60)	63(140)	27(60)	54(120)
Production rate kg/h (pounds per hour)	12.8(28.3(Est.))	20.7(45.8)	10.7(23.7(Est.))	19.4(42.8)	8.2(18.0(Est.))	21(46)
Fluidized bed volume (cubic feet)	3.9	9.8	3.6	9.5	4.2	9.2
Space/time/yield kg/h/m ³ (pounds per hour per cubic foot)	121(7.2)	79(4.7)	111(6.6)	76(4.5)	72(4.3)	84(5.0)
Residence time (hours)	2.1(Est.)	3.1	2.5(Est.)	3.3	3.3(Est.)	2.6
TEAL feed rate (cubic centimeters per hour)	110	125	113	138	166	83
Catalyst feeder (revolutions per minute)	100	-	250	-	250	-
Resin Properties	final		final		final	
Melt Index (grams per 10 minutes)	122	1.0	242	0.3	325	0.07
Flow Index	2953	145	-	59	-	11.6
Melt Flow Ratio	24.3	24	24	25	25	25
Density (gram per cubic centimeter)	0.930	0.920	0.931	0.920	0.930	0.915
Ash (weight % based on the weight of the product)	-	0.025	-	0.031	-	0.022
Bulk density of product kg/m ³ (pounds per cubic foot)	342(20.4)	319(19.0)	376(22.4)	319(19.0)	317(18.9)	302(18.0)

Example

[illegible]

Notes to Table:

1. DEAC = diethylaluminum chloride
2. THF = tetrahydrofuran
3. Total catalyst = Ti complex, i.e., titanium, magnesium, halogen, DEAC and THF; silica support; and cocatalyst
4. Residence time = average time each active catalyst particle is in the reactor.
5. Melt Index is determined under ASTM D-1238, Condition E. It is measured at 190°C.
6. Flow Index is determined under ASTM D-1238, Condition F. It is measured at 10 times the weight used in the melt index test above.
7. Melt Flow Ratio is the ratio of the Flow Index to the Melt Index.
8. The resin properties set forth under Reactor II are estimated. The resin properties set forth under final are the average values for the products of Reactors I and II.

Example 4

A modified high density polyethylene adapted for film applications is prepared. The procedure of examples 1 to 3 is repeated. The different variables follow:

Catalyst	Reactor I	Reactor II	Final Product From Reactor II
Ti loading (millimole per gram of support)	0.25	SAME	-
Mg/Ti (atomic ratio)	3		-
TEAL (weight % based on weight of silica)	5		-
Al (weight % based on weight of total catalyst)	2.88		-
Reaction Conditions			
Reactor temperature (°C)	105	30	-
Reactor pressure (psia) MPa	2.17 (315)	2.17 (315)	-
Hydrogen/ethylene (mole ratio)	0.09	0.005	-
Comonomer	1-butene	propylene	-
Comonomer/ethylene (mole ratio)	0.028	2.3	-
Ethylene partial pressure (psia) MPa	0.827 (120)	0.36 (52)	-
Percent of total production	75	25	-
Fluidization velocity m/s (feet per second)	0.45 (1.5)	0.69 (2.3)	-
TEAL (parts per million in bed)	350	350	-

Continuation of the Table on the next page

(continued)

	Catalyst	Reactor I	Reactor II	Final Product From Reactor II
5	Resin Properties			
	Melt Index (gram per 10 minutes)	0.5	0.05	0.25
	Melt Flow Ratio	30	63	90
	Density (gram per cubic centimeter)	0.950	0.865	0.928
	Average Particle Size mm (inch)	0.56 (0.022)	0.76 (0.03)	0.787 (0.031)
10	Fines (weight % based on the weight of the product - less than 120 mesh)	5	0	1.5
	Bulk density of product (pounds per cubic feet) kg/m ³	336 (20)	302 (18)	336 (20)
15	Residual Ti (parts per million)	4	1.8	3

Claims

- 20 1. A process for the in situ blending of polymers wherein a high melt index ethylene copolymer is prepared in a high melt index reactor and a low melt index ethylene copolymer is blended with said high melt index ethylene copolymer in a low melt index reactor comprising continuously contacting, under polymerization conditions, a mixture of ethylene and at least one alpha-olefin having at least 3 carbon atoms with a catalyst in the gas phase in at least two fluidized bed reactors connected in series, said catalyst comprising:
 - 25 (i) a silica supported complex consisting essentially of magnesium, titanium, a halogen, and an electron donor;
 - (ii) at least one activator compound for the complex having the formula $AlR^a_eX^fH^g$ wherein X^f is Cl or OR^m ; R^a and R^m are saturated aliphatic hydrocarbon radicals having 1 to 14 carbon atoms and are alike or different; f is 0 to 1.5; g is 0 or 1; and $e + f + g = 3$; and
 - 30 (iii) a hydrocarbyl aluminum cocatalyst, the polymerization conditions being such that a high melt index ethylene copolymer having a melt index in the range of from 0.2 to 600 grams per 10 minutes is formed in at least one high melt index reactor and a low melt index ethylene copolymer having a melt index which is lower than that of the high melt index ethylene copolymer and is in the range of from 0.001 to 1.0 gram per 10 minutes is formed in at least one low melt index reactor, each copolymer having a melt flow ratio in the range of from 22 to 70, and being admixed with active catalyst, with the proviso that:
 - 35 (a) the mixture of copolymer of ethylene and active catalyst formed in one reactor in the series is transferred to the immediately succeeding reactor in the series;
 - 40 (b) in the reactor in which the low melt index copolymer is made:
 - (1) the alpha-olefin is present in a ratio of from 0.1 to 3.5 mole of alpha-olefin per mole of ethylene; and
 - 45 (2) hydrogen is present in a ratio of from 0.001 to 0.5 mole of hydrogen per mole of combined ethylene and alpha-olefin;
 - (c) in the reactor in which the high melt index copolymer is made:
 - 50 (1) the alpha-olefin is present in a ratio of from 0.02 to 3.5 mole of alpha-olefin per mole of ethylene; and
 - (2) hydrogen is present in a ratio of from 0.05 to 3 moles of hydrogen per mole of combined ethylene and alpha-olefin; and
 - 55 (d) additional hydrocarbyl aluminum cocatalyst is introduced into each reactor in the series following the first reactor in an amount sufficient to restore the level of the activity of the catalyst transferred from the preceding reactor in the series to about the initial level of activity in the first reactor.
 2. The process defined in claim 1 wherein the activator compound is at least one of triethylaluminum, triisobutylalu-

minum, and diethylaluminum chloride.

3. The process defined in anyone of claims 1 and 2 wherein the hydrocarbyl aluminum cocatalyst is at least one of triethylaluminum and triisobutylaluminum.
4. The process defined in any one of claims 1 to 3 wherein the complex has the formula $Mg_a Ti(OR)_b X_c (ED)_d$ wherein R is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR group is alike or different; X is Cl, Br, or I, or mixtures thereof; ED is an electron donor, which is a liquid Lewis base in which the precursors of the titanium based complex are soluble; a is 0.5 to 56; b is 0, 1, or 2; c is 1 to 116; and d is 2 to 85.
5. The process defined in claim 4 wherein the electron donor is tetrahydrofuran.
6. The process defined in any one of claims 1 to 5 wherein there are two reactors in the series.
7. The process defined in any one of claims 1 to 6 wherein the melt index in the low melt index reactor is in the range of from 0.01 to 0.2 gram per 10 minutes.

Patentansprüche

1. Verfahren zum in situ-Mischen von Polymeren, in welchem ein Ethylen-Copolymer mit hohem Schmelzindex in einem Hoher-Schmelzindex-Reaktor hergestellt wird und ein Ethylen-Copolymer mit niedrigem Schmelzindex mit dem Ethylen-Copolymer mit hohem Schmelzindex in einem Niedriger-Schmelzindex-Reaktor gemischt wird, umfassend das kontinuierliche Kontaktieren unter Polymerisationsbedingungen einer Mischung von Ethylen und mindestens einem alpha-Olefin mit mindestens 3 Kohlenstoffatomen mit einem Katalysator in der Gasphase in mindestens zwei Wirbelbett-Reaktoren, die in Reihe verbunden sind, wobei der Katalysator umfaßt:

(i) einen auf einem Siliciumdioxid-Träger befindlichen Komplex, der im wesentlichen aus Magnesium, Titan, einem Halogen und einem Elektronendonator besteht;

(ii) mindestens eine Aktivator-Verbindung für den Komplex mit der Formel $AlR''_e X' f H_g$, wobei X' Cl oder OR''' bedeutet; R'' und R''' gesättigte aliphatische Kohlenwasserstoff-Reste mit 1 bis 14 Kohlenstoffatomen und gleich oder verschieden sind; f 0 bis 1,5 beträgt; g 0 oder 1 ist; und $e + f + g = 3$; und

(iii) einen Hydrocarbylaluminium-Cokatalysator;

wobei die Polymerisationsbedingungen derart sind, daß ein Ethylen-Copolymer mit hohem Schmelzindex mit einem Schmelzindex im Bereich von 0,2 bis 600 Gramm pro 10 Minuten in mindestens einem Hoher-Schmelzindex-Reaktor gebildet wird und ein Ethylen-Copolymer mit niedrigem Schmelzindex mit einem Schmelzindex, der niedriger ist als derjenige des Ethylen-Copolymers mit hohem Schmelzindex und im Bereich von 0,001 bis 1,0 Gramm pro 10 Minuten liegt, in mindestens einem Niedriger-Schmelzindex-Reaktor gebildet wird, wobei jedes Copolymer ein Schmelzflußverhältnis im Bereich von 22 bis 70 aufweist, und mit dem aktiven Katalysator gemischt wird, mit der Maßgabe, daß:

(a) die Mischung von Copolymer von Ethylen und aktivem Katalysator, die in einem Reaktor in der Reihe gebildet wird, zu dem unmittelbar darauf folgenden Reaktor in der Reihe überführt wird;

(b) in dem Reaktor, in welchem das Copolymer mit niedrigem Schmelzindex hergestellt wird:

(1) das alpha-Olefin in einem Verhältnis von 0,1 bis 3,5 Mol alpha-Olefin pro Mol Ethylen anwesend ist; und

(2) Wasserstoff in einem Verhältnis von 0,001 bis 0,5 Mol Wasserstoff pro Mol Ethylen und alpha-Olefin zusammen anwesend ist;

(c) in dem Reaktor, in welchem das Copolymer mit hohem Schmelzindex hergestellt wird:

(1) das alpha-Olefin in einem Verhältnis von 0,02 bis 3,5 Mol alpha-Olefin pro Mol Ethylen anwesend ist; und

(2) Wasserstoff in einem Verhältnis von 0,05 bis 3 Mol Wasserstoff pro Mol Ethylen und alpha-Olefin zusammen anwesend ist; und

(d) zusätzlicher Hydrocarbylaluminium-Cokatalysator in jeden Reaktor in der Reihe, der auf den ersten Reaktor folgt, in einer Menge eingeführt wird, die ausreicht, um das Aktivitätsniveau des vom vorangehenden Reaktor

in der Reihe überführten Katalysators auf etwa das Anfangsniveau der Aktivität im ersten Reaktor wiederherzustellen.

2. Verfahren nach Anspruch 1, in welchem die Aktivator-Verbindung mindestens eine von Triethylaluminium, Triisobutylaluminium und Diethylaluminiumchlorid ist.
3. Verfahren nach irgendeinem der Ansprüche 1 und 2, in welchem der Hydrocarbylaluminium-Cokatalysator mindestens eines von Triethylaluminium und Triisobutylaluminium ist.
4. Verfahren nach irgendeinem der Ansprüche 1 bis 3, in welchem der Komplex die Formel $Mg_aTi(OR)_bX_c(ED)_d$ aufweist, worin R ein aliphatischer oder aromatischer Kohlenwasserstoff-Rest mit 1 bis 14 Kohlenstoffatomen oder COR' ist, wobei R' ein aliphatischer oder aromatischer Kohlenwasserstoff-Rest mit 1 bis 14 Kohlenstoffatomen ist; jede Gruppe OR gleich oder verschieden ist; X für Cl, Br oder I oder Mischungen davon steht; ED ein Elektronendonator ist, der eine flüssige Lewis-Base ist, in der die Vorstufen des Komplexes auf Titan-Basis löslich sind; a 0,5 bis 56 beträgt; b 0, 1 oder 2 ist; c 1 bis 116 beträgt; und d 2 bis 85 ist.
5. Verfahren nach Anspruch 4, in welchem der Elektronendonator Tetrahydrofuran ist.
6. Verfahren nach irgendeinem der Ansprüche 1 bis 5, in welchem es zwei Reaktoren in der Reihe gibt.
7. Verfahren nach irgendeinem der Ansprüche 1 bis 6, in welchem der Schmelzindex in dem Niedriger-Schmelzindex-Reaktor im Bereich von 0,01 bis 0,2 Gramm pro 10 Minuten liegt.

Revendications

1. Procédé pour le mélange in situ de polymères dans lequel on prépare un copolymère d'éthylène ayant un indice d'écoulement à l'état fondu élevé dans un réacteur pour indice d'écoulement à l'état fondu élevé et on mélange un copolymère d'éthylène ayant un faible indice d'écoulement à l'état fondu avec ce copolymère d'éthylène ayant un indice d'écoulement à l'état fondu élevé dans un réacteur pour indice d'écoulement à l'état fondu faible comprenant la mise en contact en continu, dans des conditions de polymérisation, d'un mélange de l'éthylène et d'au moins une oléfine alpha ayant au moins 3 atomes de carbone avec un catalyseur, en phase gazeuse, dans au moins deux réacteurs à lit fluidisé reliés en série, ce catalyseur comprenant :
 - (i) un complexe sur support de silice essentiellement constitué de magnésium, de titane, d'un halogène et d'un donneur d'électrons;
 - (ii) au moins un composé activateur pour le complexe répondant à la formule $AlR''_eX'_fH_g$ dans laquelle X' est Cl ou OR''; R'' et R''' sont des radicaux hydrocarbonés aliphatiques saturés en C₁ et C₁₄ et sont identiques ou différents; f est 0 à 1,5; g est 0 ou 1; et e + f + g = 3; et
 - (iii) un hydrocarbyl-aluminium comme cocatalyseur, les conditions de polymérisation étant telles qu'il se forme un copolymère de l'éthylène ayant un indice d'écoulement à l'état fondu élevé, ayant un indice d'écoulement dans l'intervalle de 0,2 à 600 grammes pour 10 minutes, dans au moins un réacteur pour indice d'écoulement à l'état fondu élevé et qu'il se forme un copolymère d'éthylène de faible indice d'écoulement à l'état fondu ayant un indice d'écoulement à l'état fondu qui est inférieur à celui du copolymère d'éthylène ayant un indice d'écoulement à l'état fondu élevé, et qui est dans l'intervalle de 0,001 à 1,0 gramme pour 10 minutes, dans au moins un réacteur pour faible indice d'écoulement à l'état fondu, chacun des copolymères ayant un rapport d'écoulement à l'état fondu dans l'intervalle de 22 à 70, et étant mélangé avec du catalyseur actif, sous réserve que :
 - (a) le mélange du copolymère de l'éthylène et du catalyseur actif formé dans un réacteur de la série est transféré dans le réacteur qui le suit immédiatement dans la série;
 - (b) dans le réacteur dans lequel est préparé le copolymère de faible indice d'écoulement à l'état fondu :
 - (1) l'oléfine alpha est présente dans un rapport de 0,1 à 3,5 moles d'oléfine alpha par mole d'éthylène; et
 - (2) de l'hydrogène est présent dans un rapport de 0,001 à 0,5 mole d'hydrogène par mole d'éthylène et d'oléfine alpha combinés;
 - (c) dans le réacteur dans lequel est préparé le copolymère ayant un indice d'écoulement à l'état fondu élevé :

- (1) l'oléfine alpha est présente dans un rapport de 0,02 à 3,5 moles d'oléfine alpha par mole d'éthylène; et
 (2) de l'hydrogène est présent dans un rapport de 0,05 à 3 moles d'hydrogène par mole d'éthylène et d'oléfine alpha combinés; et

- 5 (d) un supplément de cocatalyseur à base d'hydrocarbyl-aluminium est introduit dans chacun des réacteurs de la série faisant suite au premier réacteur dans une quantité suffisante pour ramener le niveau de l'activité du catalyseur transféré du réacteur précédent de la série jusqu'aux environs du niveau initial d'activité dans le premier réacteur.
- 10 2. Procédé selon la revendication 1, dans lequel le composé activateur est le triéthylaluminium, et/ou le triisobutylaluminium et/ou le chlorure de diéthylaluminium.
3. Procédé selon l'une quelconque des revendications 1 et 2, dans lequel le cocatalyseur à base d'hydrocarbyl-aluminium est le triéthylaluminium et/ou le triisobutylaluminium.
- 15 4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le complexe répond à la formule $Mg_aTi(OR)_bX_c(ED)_d$ dans laquelle R est un radical hydrocarboné aliphatique ou aromatique en C_1 et C_4 ou COR' dans lequel R' est un radical hydrocarboné aliphatique ou aromatique en C_1 à C_4 ; les groupes OR sont identiques ou différents; X est Cl, Br ou I, ou des mélanges de ceux-ci; ED est un donneur d'électrons qui est une base de Lewis liquide dans laquelle les précurseurs du complexe à base de titane sont solubles; a est 0,5 à 56; b est 0, 1 ou 2; c est 1 à 116; et d est 2 à 85.
- 20 5. Procédé selon la revendication 4, dans lequel le donneur d'électrons est le tétrahydrofurane.
- 25 6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel il y a deux réacteurs en série.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'indice d'écoulement à l'état fondu dans le réacteur de faible indice d'écoulement à l'état fondu est dans l'intervalle de 0,01 à 0,2 gramme pour 10 minutes.